

1 "Method and Compounds"

2

3

BACKGROUND OF THE INVENTION

4

5 1. Technical Field

6

7 This invention relates to a method and compounds for
8 inhibiting corrosion in an aqueous environment and
9 particularly but not exclusively to the use of small
10 organo-sulfur molecules such as thiohydantoins as
11 corrosion inhibitors or corrosion inhibitor
12 synergists in the oil industry.

13

14 2. Discussion

15

16 Advances in drilling and completion technology have
17 revolutionised new field development and the use of
18 subsea wells with long tie backs is now common. The
19 low temperatures and long fluid transport times
20 under subsea conditions often result in a wide
21 variety of production chemistry related problems,

1 including corrosion, scale, wax and asphaltene
2 deposition, hydrate formation and bacterial growth.

3
4 A particular problem with corrosion is that it can
5 sometimes occur preferentially at welded joints.

6
7 It is known that alkyl quaternary ammonium salts can
8 be used as corrosion inhibitors and these are
9 commercially available under the brand names such as
10 DodigenTM and DodiconTM. It is thought that the
11 molecules of these salts attach to the downhole
12 metal structure - normally via a nitrogen atom
13 present in the molecule - and through a process of
14 self-assembly provide a physical barrier or film
15 between water and the structure. This film prevents
16 corrosion of the structure because the water (which
17 includes corrosion causing agents such as CO₂ and
18 H₂S) is prevented from contacting the structure.
19 Also, the organic groups present in the inhibitors,
20 being hydrophobic, repel water.

21
22 It is known that the addition of other compounds,
23 known as synergists, can significantly increase the
24 effectiveness of the corrosion inhibitors. The
25 synergists are thought to help the inhibitors bond
26 with the metal structure to provide a more effective
27 physical barrier to water.

28
29 The corrosion rates for some alkyl quaternary
30 ammonium salt corrosion inhibitors used with and
31 without synergists are shown in the table below. It
32 is shown from these results that although the

1 ammonium salt and the synergist reduce the corrosion
 2 rate moderately when used independently of each
 3 other, when used together their combination reduces
 4 the corrosion rate significantly.

| compound | corrosion rate (thousands of an inch per year ("mpy")) |
|---|---|
| blank | 32.87 mpy |
| 5ppm thiosulphate | 17.93 mpy |
| 20ppm Dodigen 2808 | 17.46 mpy |
| 20ppm Dodigen 2808+5ppm thiosulphate | 0.61 mpy |
| 20ppm Dodigen 179 | 27.40 mpy |
| 20ppm Dodigen 179+5ppm thiosulphate | 1.00 mpy |

5
 6 Thioacetamide (CH_3CSNH_2) has been identified as a
 7 persistent corrosion inhibitor/corrosion inhibitor
 8 synergist and is commonly used as such. However, it
 9 is known as a possible carcinogen.

10
 11 Sodium thiosulphate (STS) and thioglycolic acid
 12 (TGA) are also known corrosion inhibitors but suffer
 13 from the disadvantages that the former can promote
 14 pitting of stainless steels at high dose rates
 15 whilst the latter is a toxic and stench chemical.

16
 17 Substituted thiohydantoins are used in the
 18 identification of the N-terminal amino acid units of
 19 a peptide chain by means of the Edman Degradation.
 20 A free amine function bonds to a phenyl

1 isothiocyanate reagent and produces a thiohydantoin
 2 hetrocycle incorporating the N-terminal amino acid
 3 together with a shortened peptide chain.

4 Characteristic hydantoin derivatives of all the
 5 amino acids have been catalogued so identification
 6 of the terminal units is accomplished by comparison.

7
 8 Thiohydantoins are commercially available from
 9 Sigma-Aldridge and other chemical suppliers.

10

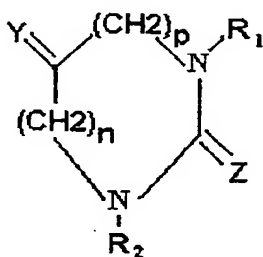
11 Thiohydantoin is not carcinogenic.

12

13 SUMMARY OF THE INVENTION

14

15 According to a first aspect of the present
 16 invention, there is provided a method of inhibiting
 17 corrosion in an aqueous environment, the method
 18 comprising the step of adding a compound according
 19 to the formula I into an aqueous environment,



20

(I)

21 wherein n is any number between 1 and 10, p is
 22 any number between 0 and 10, R₁ is H or an organic
 23 group, R₂ is H or an organic group, and Y and Z are
 24 independently any suitable atom or functional group.

25

26 The compound may be injected.

1 The invention also provides a mixture of the
2 compound defined by formula I and a carrier fluid.
3 The carrier fluid may be water, glycol or oil.
4 Preferably a mineral oil such as kerosene is used as
5 the carrier fluid.

6

7 Preferably Y is an oxygen atom or a sulfur atom.
8 Preferably Z is a sulfur atom or alternatively an
9 oxygen atom.

10

11 Preferably P is 0 or 1, more preferably 0.

12

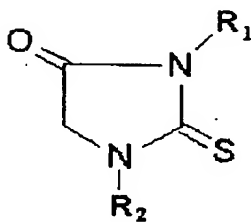
13 Preferably n is 1 or 2, more preferably 1.

14

15 Preferably the ring of formula I is a 5 or 6
16 membered ring.

17

18 More preferably the compounds of the present
19 invention are defined by formula 2



20

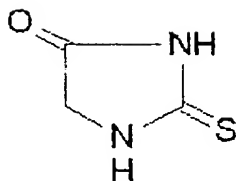
(II)

21 wherein R₁ and R₂ are independently H or an
22 organic group.

23

24 Even more preferably, the compounds of the present
25 invention are defined by formula III:

26



(III)

Preferably, the aqueous environment is part of an oilfield environment.

The aqueous environment may be any one of a cooling water system, a water flood system and a produced water system. The aqueous environment may also be in crude oil systems or gas systems and may be deployed downhole, topside, pipeline or during refining.

The aqueous environment may include CO₂, H₂S, O₂, brine, condensed water, crude oil, gas condensate, or any combination of the said or other species.

The compound may be deployed continuously or intermittently in a batch-wise manner. The compound may be used in low or high shear conditions.

The compound may be used as a corrosion inhibitor or as a corrosion inhibitor synergist in combination with an organic corrosion inhibitor.

Thus the invention also provides a mixture of a first and second compound, the mixture comprising a first compound as defined by formula I and the

1 second compound comprising an oilfield corrosion
2 inhibitor.

3
4 Examples of oilfield corrosion inhibitors for which
5 synergists are useful include amines, amido amines,
6 quatazamines, imidazolines, amides, ethoxylated
7 amines, quaternary ammonium salts, betaines,
8 phosphate esters, sulphonates, polyaspartates, fatty
9 acids, glycols such as mono-, bi, and tri-
10 ethyleneglycol. Oligomers and polymers of these
11 corrosion inhibitors may also be used with the
12 compound.

13
14 The compounds of the present invention may also be
15 used as part of a combined product, i.e. corrosion
16 inhibitor combined with scale inhibitor, wax
17 inhibitor, hydrate inhibitor, demulsifier, deoiler
18 or any other corrosion inhibitor.

19
20 When used as a synergist, R_1 and R_2 are preferably
21 organic groups such as alkyl groups. Preferably R_1
22 and R_2 comprise between 1 and 40 carbon atoms.
23 Certain known synergists comprise carbon chains of
24 around 18 carbon atoms thus R_1 and R_2 preferably have
25 around 18 carbon atoms.

26
27 According to a further aspect of invention, there is
28 provided a compound for use as a corrosion inhibitor
29 as defined by formula I.

30

1 The invention also provides the use of a compound as
2 defined by formula I as a corrosion inhibitor or as
3 a corrosion inhibitor synergist.

4

5 The invention also provides a corrosion inhibitor or
6 corrosion inhibitor synergist, comprising a compound
7 as defined by formula I.

8

9 Embodiments of the invention will now be described
10 by reference to the following examples.

11

12 DETAILED DESCRIPTION OF THE INVENTION

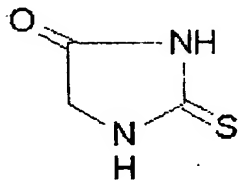
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14 In order to investigate the efficiency of corrosion
15 inhibition by thiohydantoin, aqueous linear
16 polarisation resistance (LPR) bubble tests were
17 carried out and compared with thioacetamide.
18 Thiohydantoin is not carcinogenic. As the basic
19 structure of thiohydantoin is similar to imidazoline
20 it was also compared against 2-methyl-2 imidazoline
21 a similar sulfur free imidazoline.

22

23 The structures of 2-thiohydantoin, thioacetamide and
24 2-methyl-2-imidazoline are shown below:

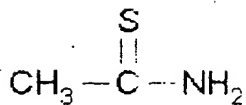
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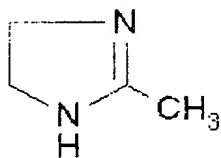
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27

2-thiohydantoin



thioacetamide



2-methyl-2-imidazoline

The procedure for conducting the bubble test is generally based on a protocol developed by BP Sunbury and described in "Corrosion Inhibitor Test Methods", S Webster, A J McMahon, D M E Paisley, D Harrop, BP Sunbury report ESR.94.ER.054, dated November 1996 and also "Corrosion Inhibitor Guidelines", A J McMahon, S Groves, BP Sunbury report ESR.95.ER.050, dated 1996.

The procedure also makes use of principles from the following ASTM standards,

- G1-90 (1999) "Standard Practise for Preparing, Cleaning and Evaluating Corrosion Test Specimens"
- G102-89 (1999) "Standard Practice for Calculation of Corrosion Rates and Related Information from Electrochemical Measurements"
- G5-94 (1999) "Test Method for Making Potentiostatic and Potentiodynamic Anodic Polarization Measurements"

1

2 • G59-97 "Standard Practice for Conducting
3 Potentiodynamic Polarization Resistance
4 Measurements"

5

6 • G61-86 (1998) "Standard Test Method for
7 Conducting Cyclic Potentiodynamic Polarization
8 Measurements for Localized Corrosion Susceptibility
9 of Iron-, Nickel-, or Cobalt-Based Alloys".

10

11 The bubble test involves a carbon steel electrode
12 immersed in a bath of oilfield brine, and possibly a
13 crude oil, to simulate the environment in which the
14 corrosion inhibitor would be used. A gas, commonly
15 CO₂, which is a corrosion causing agent, is bubbled
16 through the brine mixture and the corrosion rate of
17 the electrode in the absence of a corrosion
18 inhibitor is measured using the linear polarisation
19 resistance method (LPR) or AC Impedance (EIS). The
20 inhibitor under examination is then added, normally
21 after two hours, and the subsequent polarisation
22 resistance/ corrosion rate is recorded. This data
23 can be used to calculate the inhibitor efficacy.

24

25 Results

26

27 Aqueous bubble tests were carried out on the three
28 inhibitors/synergists in duplicate.

1

| Inhibitor | Dose (ppm) | Corrosion Rate (mpy) | | % Inhibition |
|------------------------|---------------|-------------------------|-----------------|--------------|
| | | Before inhib. | After inhib. | |
| Thioacetamide | 1 | 144.96 | 5.58 | 96.15 |
| Thioacetamide | 1 | 152.60 | 3.55 | 97.67 |
| Thiohydantoin | 1 | 163.47 | 18.07 | 88.95 |
| Thiohydantoin | 1 | 141.09 | 9.42 | 93.32 |
| 2-methyl-2-imidazoline | 1 | 146.81 | 216.65 | 0 |
| 2-methyl-2-imidazoline | 1 | 144.07 | 193.81 | 0 |

2

3 **Table 1 : Aqueous Bubble Test Results using 3% NaCl**
 4 **at 50°C**

5

6 In these tests the thiohydantoin did not perform as
 7 well as thioacetamide. Methyl imidazoline performed
 8 poorly as the corrosion rate actually increased,
 9 from 145mpy to 200mpy and therefore it was decided
 10 not to continue testing with this product.

11

12 The aqueous bubble tests were repeated using BP
 13 Forties synthetic brine and the results are shown in
 14 table 2. In this test the performances of
 15 thioacetamide and thiohydantoin had improved with a
 16 significant improvement in the result from
 17 thiohydantoin when compared to the bubble test with
 18 3% NaCl. This is thought to be due to the presence
 19 of other trace ions in the Forties brine.

20

| Inhibitor | Dose (ppm) | Corrosion Rate (mpy) | | % Inhibition |
|---------------|---------------|-------------------------|-----------------|-----------------|
| | | Before inhib. | After inhib. | |
| Thioacetamide | 1 | 146.84 | 1.29 | 99.12 |
| Thioacetamide | 1 | 208.29 | 0.82 | 99.61 |
| Thiohydantoin | 1 | 174.73 | 1.64 | 99.06 |
| Thiohydantoin | 1 | 132.10 | 1.07 | 99.19 |

Table 2 : Aqueous Bubble Test Results using Forties
Synthetic Brine at 50°C

Partition bubble tests were performed on thioacetamide and thiohydantoin. In this test 600ml of brine is first added to a test cell. A mixture of a further 200 ml brine and 200 ml crude oil is made up and thoroughly mixed before being added to the brine in the test cell.

The fluids used in the partition bubble tests were Forties synthetic brine and Forties crude oil. 800ml of brine and 200ml of crude were used to investigate the partition efficiency of the inhibitors and the results are shown in table 3 below.

1

| Inhibitor | Dose (ppm) | Corrosion Rate (mpy) | | % Inhibition |
|---------------|---------------|-------------------------|-----------------|-----------------|
| | | Before inhib. | After inhib. | |
| Thioacetamide | 1 | 241.36 | 0.97 | 99.60 |
| Thioacetamide | 1 | 211.37 | 0.70 | 99.67 |
| Thiohydantoin | 1 | 239.59 | 2.41 | 98.99 |
| Thiohydantoin | 1 | 202.79 | 1.35 | 99.33 |

2 Table 3 : Partition Bubble Test Results using
3 Forties Synthetic Brine at 50°C

4

5 The performance of thioacetamide and thiohydantoin
6 was similar to that achieved under aqueous Forties
7 conditions. (Table 2) Thus, it can be seen that
8 thiohydantoin gives effective corrosion inhibition
9 in aqueous and partitioning bubble tests. The
10 thiohydantoin offers similar or better performance
11 than thioacetamide.

12

13 Thiohydantoin was evaluated further as a corrosion
14 inhibitor and as a corrosion inhibitor synergist
15 using a rotating cylinder electrode (RCE) test at
16 5000rpm (29.5 Pa) The rotating cylinder electrode
17 test comprises a rotating carbon steel electrode
18 immersed in a bath of oilfield brine and possibly
19 crude oil to simulate the shear stresses that may be
20 encountered in the environment which the corrosion
21 inhibitor would be used. In certain tests, pre-
22 partitioning of the inhibitor is carried out with
23 brine/crude shaken with inhibitor present and the
24 separated brine used for the tests. A gas, commonly

1 CO₂, is bubbled through the brine mixture and the
 2 electrode rotation started at the required rate.
 3 The corrosion rate of the brine is then measured
 4 using the linear polarisation resistance method
 5 and/or AC impedance. If unpartitioned brine is used
 6 the inhibitor being tested is added at this point
 7 and the inhibitor rate measured. If partitioned
 8 brine is used the initial rate is the inhibitor
 9 corrosion rate and is compared to partitioned brine
 10 without inhibitor to calculate the inhibition ratio.
 11
 12 The results are shown in Table 4.

| Inhibitor | Dose (ppm) | Corrosion Rate (mpy) | | % Inhibition |
|---------------------------------------|---------------|-------------------------|-----------------|-----------------|
| | | Before inhib. | After inhib. | |
| thiohydantoin | 1 | 160.50 | 4.65 | 97.10 |
| thiohydantoin | 1 | 90.01 | 11.24 | 87.51 |
| Thiohydantoin (1ppm) + QUAT (2ppm) | 3 | 91.76 | 2.80 | 96.95 |
| Thiohydantoin (1ppm) + QUAT (2ppm) | 3 | 90.06 | 5.59 | 93.79 |

13
 14 Table 4 : Rotating Cylinder Electrode Test using
 15 3%NaCl Brine at 50°C. (QUAT=quaternary ammonium
 16 salt.)

17
 18 Thus it can be seen that thiohydantoin, on its own,
 19 or in combination with a quaternary ammonium salt
 20 corrosion inhibitor gives effective corrosion
 21 inhibition in pre-partitioned shear conditions.
 22

1 The quantity of thiohydantoin used in the
 2 formulation with the QUAT is the same as in previous
 3 tests. The QUAT is CLARIANTTM Dodigen 2808, a coco
 4 benzyl quat.

5
 6 A further RCE test was used to investigate the
 7 persistency of thiohydantoin. The brine was
 8 replaced with fresh brine after 20 hours. Although
 9 some persistency was observed the corrosion rate
 10 increased from 11mpy to 35 mpy and the results are
 11 shown in Table 5.

12

| Inhibitor | Dose (ppm) | Corrosion Rate (mpy) | | |
|---------------|---------------|----------------------|-----------------|----------------|
| | | % Inhibition | | |
| | | Before inhib. | After inhib. | Fresh brine |
| Thiohydantoin | 1 | 90.01 | 11.25 | 35.45 |

13

14 Table 5 : Persistency Test using 3%NaCl Brine at
 15 50°C

16

17 Thus thiohydantoin offers some corrosion inhibition
 18 when tested for film persistency.

19

20 In order to test the efficacy of thiohydantoin with
 21 respect to inhibiting weld corrosion, aqueous bubble
 22 tests were carried out using four 1% Nickel
 23 segmented weld electrodes on thiohydantoin and an
 24 amine based corrosion inhibitor. The whole weld is
 25 referred to in the art as a "weldment" and comprises
 26 the main part of the weld, Heat Affected Zones
 27 (HAZs) of the two parts being joined together on

- 1 either side of the weld. On either side of these
- 2 zones, the weldment comprises 'Parent' portions.

1

| I | Corrosion Rate | | | | |
|--------|----------------|-------|----------|--------|------------|
| | Inhibitor | Dose | Baseline | Inhibi | % |
| | | (ppm) | (mpy) | ted | Inhibition |
| | | | | (mpy) | |
| Weld 3 | Thio- | 1 | | | |
| | hydantoin | | | | |
| Weld | | | 21.35 | 11.02 | 48.6 |
| HAZ 1 | | | 212.74 | 109.24 | 34.2 |
| HAZ 2 | | | 203.34 | 133.76 | 73.2 |
| Parent | | | 221.84 | 59.36 | 77.2 |
| 1 | | | | | |
| Parent | | | 248.6 | 56.77 | 38.9 |
| 2 | | | | | |
| Weld 4 | Thio- | 1/20 | | | |
| | hydantoin | | | | |
| | /amine | | | | |
| | inhibitor | | | | |
| Weld | | | 66.5 | 40.61 | 67.9 |
| HAZ 1 | | | 213.43 | 68.33 | 32.0 |
| HAZ 2 | | | 199.2 | 135.42 | 46.7 |
| Parent | | | 29.46 | 15.68 | 46.6 |
| 1 | | | | | |
| Parent | | | 28.7 | 15.31 | 46.6 |
| 2 | | | | | |

2 Table 6 Aqueous Bubble Test Results using Forties
3 Synthetic brine at 50°C

4

5 Thus it is shown from these results that
6 thiohydantoin, particularly when mixed with an amine
7 inhibitor has been shown to be inhibiting corrosion

1 at weldments, which often corrode preferentially to
2 other parts of a metal structure.

3
4 On the basis of these tests thiohydantoin is a
5 viable and non-carcinogenic alternative to
6 thioacetamide. Thiohydantoin matches the excellent
7 corrosion inhibition of thioacetamide in a series of
8 static and dynamic tests. Indeed, it is considered
9 that thiohydantoin is suitable to be used as a
10 corrosion inhibitor in its own right. In such
11 cases, the hydrogens attached to the nitrogen atoms
12 may be replaced by organic or alkyl groups of the
13 order of C_1 - C_{40} but preferably around C_{18} .

14
15 A six membered ring equivalent such as a pyrimidine
16 based ring is also effective against corrosion
17 inhibition.

18
19 Thiohydantoin (and derivatives) are also effective
20 against other known corrosion causing agents, such
21 as H_2S .

22
23 Thus the present invention provides an easily
24 available range of compounds for use as corrosion
25 inhibitors or corrosion inhibitor synergists which
26 have a similar efficacy to thioacetamide.

27
28 Modifications and variations may be made without
29 departing from the scope of the invention.